

# **Report for 2004ME29B: Metal mobilization from municipal biosolids stockpiles: The role of dissolved organic matter.**

## **Publications**

- Articles in Refereed Scientific Journals:
  - Peckenham, J.M., J. Nadeau and A. Amirbahman (2005)  
Nitrogen Release from Field Stack Biosolids, BioCycle, 46, pp. 47-52.

## **Report Follows**

# **Release of Nitrogen and Trace Metal Species from Field Stacked Biosolids**

**Aria Amirbahman<sup>1</sup>, John Peckenham<sup>2</sup>, James Nadeau<sup>1</sup>, and Richard Behr<sup>3</sup>**

<sup>1</sup> Department of Civil and Environmental Engineering, University of Maine, Orono, ME 04469.

<sup>2</sup> Senator George J. Mitchell Center for Environmental and Watershed Research, University of Maine, Orono, ME 04469.

<sup>3</sup> Maine Department of Environmental Protection, Augusta, ME 04333.

## **Abstract**

The goal of this study was to measure the amount and speciation of nitrogen (N) and metals leaving stockpiled biosolids and traveling through soil column. Biosolids were placed on plastic lined cells to collect all leachate. Ammonium ( $\text{NH}_4^+$ ) was the dominant species (90% of total N) released from the Class B lime-stabilized biosolids in the lined cell experiment.  $\text{NO}_3^-$  and nitrite ( $\text{NO}_2^-$ ) concentrations were essentially negligible, remaining below  $0.25 \text{ mg L}^{-1}$  and  $0.1 \text{ mg L}^{-1}$ , respectively.  $\text{NH}_4^+$  levels ranged from 2,000 to  $4,900 \text{ mg L}^{-1}$  in the leachate. Dissolved organic carbon (DOC) concentrations as high as  $8,900 \text{ mg L}^{-1}$  and chemical oxygen demand (COD) as high as  $37,000 \text{ mg L}^{-1}$  were measured in the leachate leaving the lined cell. Fifteen pan lysimeters were installed in an  $90 \text{ m}^2$  plot at depth intervals of 30, 60, and 100 cm. Leachate passing through the soil column underlying the biosolid stockpile was collected in the zero tension pan lysimeters. Average lysimeter  $\text{NH}_4^+$  concentrations ranged from  $1,400 \text{ mg L}^{-1}$  at 60 cm depth to  $145 \text{ mg L}^{-1}$  at 90 cm depth. Average lysimeter DOC concentrations ranged from  $2,000 \text{ mg L}^{-1}$  at 60 cm to  $525 \text{ mg L}^{-1}$  at 90 cm. At day 30, the cumulative loading of N species from the lined-cell was 20 times typical agronomic levels.

Trace metal determinations of the leachates collected from the lined cell and lysimeters showed arsenic loading rates exceeded the MRSA Chapter 419 limits of  $0.5 \text{ kg ha}^{-1} \text{ yr}^{-1}$  by an order of magnitude. Arsenic concentrations were in excess of several thousand  $\text{mg L}^{-1}$  in the lined-cell leachate and several hundred  $\text{mg L}^{-1}$  in the lysimeters as deep as 90 cm under the biosolid stockpile. Phosphorus, iron and manganese in excess of several thousand  $\text{mg L}^{-1}$  were observed in both the lined-cell leachate and lysimeters. Significant concentrations of other trace metals were found at depth in the zero-tension lysimeter plot. Trace metals were largely mobilized by the DOC from the biosolids, and/or due to the presence of anaerobic environment, especially in the underlying soil.

## **Introduction**

Biosolids are derived from sewage sludge and have been treated to meet specific land-application criteria in accordance with the US EPA part 503 rules developed in 1993 to ensure safe agronomic use. Sewage sludge contains pathogens and biosolids are defined by the processing method used to reduce pathogen content. Class A biosolids have been treated to reduce pathogens to natural background concentrations. Class B biosolids have been treated to reduce pathogens, but not to background concentrations. The uses of Class B biosolids are restricted by well-defined site suitability and access control regulations; land application is a primary outlet for this class.

Field application of biosolids, especially in agricultural areas, is practiced widely (Stevens et al., 2002; Wang, 1997). Field stacking of biosolids prior to their application is an allowed practice in many countries and states, under local licensing standards, enforcement rules and regulations. Field stacking of biosolids is necessary to accommodate cropping schedules and in northern climates where land application is precluded during the winter season (USEPA, 2000). Field stacking allows for efficiency of operation at the farm as hundreds to thousands of m<sup>3</sup> of material can be stored and then applied in one application. Field stacking is typically done in agricultural areas that are remote from public access and may occur on bare ground (USEPA, 2000; Peckenham, 2004).

Biosolids generated in Maine (USA) contain nutrients such as: nitrogen (0.1 to 8%), phosphorus (0.1 to 3.2%), and potassium (0.0 to 0.8%) (Peckenham, 2005). Biosolids may also contain trace metals in concentrations > 100 ppm; e.g. Chromium, Copper, Iron, Lead, Manganese, Nickel, and Zinc, and a variety of other metals in lower concentrations (Cappon, 1984; Bell et al., 1991; Basta, 2005; McBride et al., 2004). Field application of biosolids, both as amendments and for storage purposes, can therefore, result in the release of nutrient and metal species into the surrounding environment (Gerritse et al., 1982; Clapp et al., 1994; McBride et al., 1997; Shober et al., 2002). Elevated NO<sub>3</sub><sup>-</sup> levels in groundwater surrounding agricultural and grazing lands are well documented (Smith et al., 1998a, b; Maticic, 1999; Smith and Frost, 2000; Maeda et al., 2003). However, there is little information about the release of NO<sub>3</sub><sup>-</sup> from biosolids stockpiles. Leaching of NO<sub>3</sub><sup>-</sup> from biosolids stockpiles was suggested as the source of nitrogen plumes measured in a gravel pit reclamation site, and also from repeated stacking of chicken manure at the same site was reported (Hillier, 1993; McDowell and Chestnut, 2002). Even

though some studies have reported the significant impacts of manure stockpiling and cattle slurry lagoons on groundwater quality (Gooddy et al., 2002), research that exclusively measured the N losses from field stacked biosolids is lacking.

Trace metal release from biosolids has been linked to microbiological activity (Qureshi et al., 2003), water solubility (McBride, 1998) and breakdown of organic compounds that bind metals in the soil (Martinez et al., 2003). McBride et al. (1999) showed that shallow groundwater collected via tension lysimeters from an experimental plot that had a single high-dosage application of biosolids 15 years prior had elevated levels of several trace metals when compared to a nearby control plot that had received no biosolids application. Richards et al. (1998) found elevated trace metal levels such as cadmium (Cd), nickel (Ni), zinc (Zn) and boron (B) in soil pore water of a site treated with biosolids 20 years earlier. The evidence of increased trace metal concentrations in waters surrounding biosolids application sites, including a 20-year long watershed scale experiment in Minnesota (Clapp et al., 1994), is mixed due to natural heterogeneity of soils, uncertainties in biosolids compositions, and lack of control sites (Gerritse et al., 1982; Stukenberg et al., 1993; Berti and Jacobs, 1998; Babarick et al., 1998; Sloan et al., 2000; National Research Council, 2002).

## **Materials and Methods**

**Plot Designs:** Two experimental plots were constructed and stacked with municipal biosolids at the University of Maine's research farm. The local soils are formed in a dense glacial till, Marlow silt loam (coarse loamy isotic frigid oxyaquic Haplorthod) and Woodbridge silt loam (coarse loamy mixed mesic aquic Dystrudept) that meets Maine's stockpiling suitability criteria for slope (<5%), drainage class (moderately well-drained), and texture (silt loam).

The plots consisted of: (1) a pair of lined cells designed to capture and measure all leachate and runoff generated, and (2) a zero-tension pan lysimeter plot designed to capture flow through the soil beneath field-stacked biosolids. The design of the lined cell and the lysimeters is described in detail elsewhere (Peckenham et al, 2005). Briefly, one  $3.6 \times 22.5$  m cell and one  $1.8 \times 30.5$  m cell were constructed by removing the vegetation and sloping the base inward. A 1.27 mm thick impermeable PVC sheet was cut to size and placed over the base area. A slotted flexible plastic pipe was placed along the centerline to collect the leachate from the pile. The PVC barrier and the drain pipe were covered with 12 – 18 cm of fine sand to facilitate flow of the leachate. Lime-stabilized class-B biosolids were stacked to a depth of 0.6 to 0.8 m as unloaded from truck or tractor bucket.

The water, or snow melt, shed from stockpile surfaces was collected using an open pipe system placed along the perimeter of the stockpile. The leachate and runoff flow rates were measured using 90° v-notch weirs and flow meters (ISCO® 4230). The leachate samples were collected with auto-samplers that were triggered by the flow meters and collected a 100 ml sample for every 100 L of flow (Peckenham et al, 2005).

The zero-tension pan lysimeter plot was  $6 \times 15$  m, and consisted of fifteen  $45 \times 45 \times 5$  cm stainless steel pan lysimeters. Placement of the lysimeter pans at depth was accomplished by digging a 0.6 m wide trench to the desired depth (0.3, 0.6, and 1 m), placing the pans, collection bottles and sampling tubes in place, then filling the trench with the material that was originally removed (Figure 1). The lysimeters were individually drained into buried polyethylene containers. Samples were collected using a manual vacuum pump. Lime-stabilized biosolids were stacked to a maximum thickness of ~1 m.

The stockpiling experiments for both the lined cell and the lysimeters were performed twice. The first stockpile was in place from December 2002 to May 2003, and consisted of 125 m<sup>3</sup> of biosolids to the lined cells and 90 m<sup>3</sup> to the lysimeter plot. In this run, freezing

temperatures made flow quantification difficult to impossible. The second stockpile was in place from July 2003 to May 2004 and consisted of 52.5 m<sup>3</sup> of biosolids to the lined cell and 90 m<sup>3</sup> to the lysimeter plot. The road sand on the bottom of the lined cell was allowed to be rinse by several rain storms between stackings, while the lysimeter plot was scraped and aerated for 30 days then restacked.

**Sampling Methods.** Composited biosolids samples were collected for analysis immediately after the stacking and just before the removal of biosolids at the completion of each stacking period. Composited samples consisted of 10 individual samples, collected utilizing a three-dimensional random grid approach. Composited biosolids were mixed in a bucket by hand and then re-sampled. The biosolids were analyzed as shown in Table 1.

Composited soil samples from beneath the lysimeter plot were collected before and after stockpiling and analyzed as shown in Table 1. All composited samples consisted of 10 individual samples, collected utilizing a random grid approach using a soil sampling tube (25.4 cm). All soil and biosolids samples were stored on ice during transportation and kept at 4° C until analyzed (within 7 days).

Data reported here are for the second stockpiling experiment. Aqueous samples from the lined cells were collected from the auto-samplers every 3 to 14 days. The individual 500 ml polyethylene bottles in the auto-samplers were transferred into Whirl-Pak<sup>®</sup> bags, placed on ice in coolers and transported to the lab. The aqueous samples were analyzed as shown in Table 1. Daily rain fall information, collected at the farm, was used in this study. Four field rain gauges were deployed in the experimental field to verify farm precipitation data.

The lysimeters were sampled approximately monthly from June 2003 to October 2003. Additional samples were collected in May and July 2004. Samples from each individual lysimeter were placed in an acid-washed 500 ml polyethylene bottle. The bottles were kept on ice until transferred to the lab for analysis. The remaining liquid in the submerged containers was completely drained after each sampling event. Dissolved organic nitrogen was determined by subtracting the concentrations of NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup> and NO<sub>2</sub><sup>-</sup> from total Kjeldahl nitrogen (TKN).

**Analytical Methods.** Laboratory pH was measured using a Corning Model 430 meter with an Orion Model 8104-BN probe. Field pH measurements were performed using a Hach pH pen calibrated at pH 4 and 7. Biosolids pH was determined by adding 70 ml of DI water to

approximately 35 ml of biosolids in a Nalgene® bottle. The bottle was capped, thoroughly shaken and pH of the slurry measured after 15 min.

Samples for  $\text{NH}_4^+$  measurement were filtered through 0.45  $\mu\text{m}$  polypropylene filters and acidified to a pH of 2.0 with 1:1  $\text{H}_2\text{SO}_4$ .  $\text{NH}_4^+$  was analyzed on an ALPKEM Flow Solution™ IV Automated Analyzer using the Berthelot reaction [EPA Method 353.2]. Nitrate was measured calorimetrically after its reduction by cadmium to  $\text{NO}_2^-$  at pH 7.5, while nitrite was determined directly without the reduction step. Total Kjeldahl Nitrogen (TKN) was determined on approximately 5 ml of leachate or 5 g of biosolids. Solids were dried at 105°C to remove adsorbed moisture. Samples were digested in a mixture of sulfuric acid, potassium sulfate and cupric sulfate at 400° C for 1 hr to convert amino-nitrogen from most organic materials into  $\text{NH}_4^+$ . Free  $\text{NH}_3$  was also converted to  $\text{NH}_4^+$ . The digested sample was concentrated by heat distillation into a standardized acid in a receiving flask. Total Nitrogen was quantified as ammonium by neutralization with a standardized NaOH solution.

Organic carbon in the leachate, runoff and lysimeter samples were determined using an OI Analytical Model 1010 Total Carbon Analyzer. Chemical oxygen demand was determined using Hach Method 430/435, Hach COD reactor Model 45600 and a DR/2000 spectrophotometer. Percent solids were determined gravimetrically after heating the samples for 24 hours at 110° C. Loss on ignition (LOI) of the solid samples was determined by heating the samples at 550° C in a muffle furnace for 3 hours.

Metal concentrations were measured on an ICP-AES (Perkin-Elmer Optima 3300XL), after filtering through 0.45  $\mu\text{m}$  membranes. Standard additions of a stock solution with known metal concentrations were made to a leachate sample to test the matrix effect on the ICP-AES measurements.



## **Results and Discussion**

### **Liquid Release from Biosolids**

The biosolids stockpile generated negligible volumes of leachate for several days (10 to 14 days), then leachate flux increased and peaked at ~60 days followed by a gradual decline. No measurable runoff was generated as all liquid on the surface either flowed into the biosolids or was evaporated. The predicted leachate volume was calculated from available precipitation data (not shown here) and a collection area of 81 m<sup>2</sup> with no surface runoff or evaporation. During the first three weeks, the leachate volume produced was less than the precipitation input. After three weeks, leachate volume increased in excess of precipitation input and remained in excess for nearly two months. The initial lag between the measured and the calculated leachate volume may be attributed to the absorption of water by the newly stockpiled biosolids. Eventually the stockpiled biosolids released the stored liquid with a net increase in total solids from 25.8% to 31.0 %. The total volume of leachate released was approximately 40,000 liters.

### **Leachate Chemistry-Nutrients and pH**

Concentrations of N species, DOC and COD in the leachate are shown in Table 2. The dominant N species was  $\text{NH}_4^+$  with maximum concentrations exceeding 4800 mg/L.  $\text{NO}_3^-$  and  $\text{NO}_2^-$  concentrations remained below 0.21 mg/L and 0.07 mg/L, respectively, constituting a very small fraction of total N. On average, dissolved organic nitrogen (DON) represented approximately 10% of the total N released. All nitrogen species' concentrations increased over time. COD and DOC concentrations were greatest at day 36 at 37,000 and 8,900 mg/L, respectively. This was followed by a slow and steady decrease for the remainder of the experimental period. The dissolved oxygen (DO) concentration was measured at the collection point for the auto-sampler (where the leachate drained into a collection bucket) with a portable field meter during several rain events, and was consistently <0.1 mg/L.

Application rates of land-applied biosolids are regulated to account for N demand of crops. When calculating these application rates, the percent inorganic (mineral) N and organic N in the biosolids are considered. Approximately 90% of the total N in the leachate is mineral ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$ ). Comparing an average crop value of 225 kg/ha nitrogen demand with the calculated loadings shows that the agronomic demands at the stockpile are exceeded by a factor of approximately 20 in the first 30 days of stockpiling. This factor increases to

approximately 60 and 70 times agronomic demands at 60 and 90 days, respectively. The loss of N from biosolids stockpiles exceeds agronomic demand and will likely lead to N saturation in the soil near the stockpile with subsequent losses of  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{NO}_2^-$  into groundwater (Jacobsen, 1998; Smith et al. 1998a, b; Roelle et al., 2002).

The biosolids composition changed during the second experiment with a net decrease in organic carbon as estimated by LOI from 27.6 weight % to 24.9 weight %, an insignificant decrease in  $\text{NH}_4^+$  (2500 to 2300  $\text{mg kg}^{-1}$ ), a net decrease in  $\text{NO}_3^- + \text{NO}_2^-$  (6.7  $\text{mg kg}^{-1}$  to 2.5  $\text{mg kg}^{-1}$ ) and a net decrease in TKN (3.2 weight % to 0.9 weight%). Calculating the carbon loss by difference, based on the biosolids analyses, shows a 350 kg loss from the stockpile compared to a calculated loss of 290 kg based on the leachate composition. The same calculations show an N loss of 240 kg based on biosolids analysis compared to 145 kg N loss based on the leachate. This discrepancy may be largely attributed to the production of gaseous  $\text{CO}_2$  and  $\text{N}_2$  due to the mineralization of the organic matter and microbially-catalyzed denitrification. Release of  $\text{CO}_2$  and  $\text{N}_2$  from biosolids-amended soils have been estimated at between 10 and 25% of the total released from the biosolids (Smith et al., 1998a, b; Balint et al., 2002; Roelle et al., 2002).

Lime was added to the biosolids to increase pH to ~12. Calcium loss and pH decline are closely correlated as shown in Figure 2. Calcium concentrations in the leachate reached a maximum of 1,000  $\text{mg/L}$  near day 20, then rapidly decreased to  $<100 \text{ mg/L}$ . The pH declined simultaneously from  $>11$  to approximately 7.5 during this same time period.

### **Leachate Chemistry – Trace Metals**

Time-series trends in concentrations of selected metals (Al, As, Cd, Cu, Fe, Mn, Ni, Se, and Zn) and P in the leachate of lined cells are shown in Figure 3. Leachate Fe and Mn concentrations peak at 130 and 17  $\text{mg L}^{-1}$ , respectively, by day 20, after which they decreased. For Fe, the concentration began to increase slowly after day 40. Leachate Mn concentration, however, remained very low after day 30. It is likely that Fe and Mn are released during microbially-catalyzed reductive dissolution of their respective oxyhydroxides that happens under anoxic conditions typical of the environment inside the stacked biosolids (Lovley and Phillips,

1988). The sharp drop in the concentrations observed after day 20 may be due to the depletion of the available Fe- and Mn-oxyhydroxides (von Gunten and Zobrist, 1993; Amirbahman et al., 2003), and the increase in the Fe concentration after day 40 may be due to the slow dissolution of the more crystalline Fe-containing minerals. The pH decrease to a circumneutral value (Fig. 2) coincides especially with the drop in Mn concentration. Mn minerals are quite insoluble at both alkaline and circumneutral pH values regardless of the redox potential (Krauskopf and Bird, 2003), and as such, it is unlikely that changes in biosolids pH as reported here would result in significant mobilization or removal of Mn. Also, precipitation of rhodochrosite ( $\text{MnCO}_{3(s)}$ ) is favored at high pH, whereas in this study, Mn is mobile at a high pH.

Leachate Al, As, P, Zn and Cd concentrations were relatively constant for nearly the first 50 days, after which they increased (Fig. 4). By day 100, As, Al, P, Zn and Cd concentrations were nearly 2.5, 2, 8, 0.2 and 0.015  $\text{mg L}^{-1}$ , respectively. The concentrations of these species do not directly correlate with that of Fe and Mn, and therefore, it is not likely that their mobilization is directly related to the mobilization of Fe and Mn. Considering the relatively strong affinity of these species especially with the Fe(III) (oxy)hydroxide surface (Dzombak and Morel, 1990), this lack of correlation with Fe may be attributed to the strong interaction of DOC with Fe colloids that results in the coverage of their reactive surface sites, and complexation of the species with DOC. The lack of correlation between the abrupt drop in pH observed between days 20 and 30 and release of these species also suggests that pH drop is not directly responsible for their release from the biosolids. One possible mechanism for the release of Al, As, P and Zn may, therefore, be due to the mineralization of organic matter with time.

Aluminum is mostly believed to be non-colloidal. However, considering the solubility of gibbsite ( $\text{Al}(\text{OH})_{3(s)}$ ), free Al concentration at a circumneutral pH should be  $< 1 \mu\text{g L}^{-1}$  (Stumm and Morgan, 1996), and therefore, Al is largely complexed by the fulvic acid or the low molecular weight organic acid fractions of DOC. Association of metal cations such as Zn and Cd with DOC is well-documented (Tipping, 2002). Redman et al. (2002) and Lin et al. (2004) observed complexation of As with DOC, especially in the presence of bridging cations, such as Fe. Therefore, As in the leachate may be truly dissolved or associated with DOC. P is also expected not to be associated with the Fe and Mn colloids. Soluble P, however, may possibly

have a direct microbial association and be part of large biomolecules or associated with the DOC via bridging cations.

Concentrations of Cu and Ni were approximately  $1 \text{ mg L}^{-1}$  on day 6 and reduced to approximately  $0.4 \text{ mg L}^{-1}$  after that and remained relatively constant over the duration of the experiment. Selenium concentration remained relatively constant at approximately  $0.17 \text{ mg L}^{-1}$  until day 25 after which it consistently declined to approximately  $0.03 \text{ mg L}^{-1}$  by day 100.

Jensen and Christensen (1999) studied the physical size and colloidal nature of metals found in leachate from landfills. Their findings agree well with those of this study, where they observed that nearly 80-95% of Cd, Cu, K, Mg, Na, Ni, Pb and Zn were  $< 1 \text{ K Da}$ , while nearly half of Ca and Mn were  $< 1 \text{ K Da}$ , and Fe was 85%  $> 1 \text{ K Da}$ .

### **Lysimeter – Nitrogen Species**

The average concentrations of N species DOC at various lysimeter depths are shown in Figure 4. Figure 4 depicts time-series trends for samples taken at 30, 60 and 90 cm depths at four different sampling dates. The June 2003 samples were collected after the removal of the first stockpile that was in place for six months, and before the emplacement of the second stockpile, which lasted from July 2003 to May 2004. The second date, September 2003, and third date, May 2004, were collected when the second stockpile was in place, and the fourth date, July 2004, was collected two months after the removal of the second stockpile.

Average DOC concentrations at 30 cm and 60 depths range between 1000 and 4000  $\text{mg kg}^{-1}$ . DOC concentrations show a marked increase at all three depths from June to September 2003. This may be attributed to the fresh biosolids stockpile emplaced in July 2003. The average DOC increases consistently with time at a depth of 90 cm. The DOC concentrations are consistently higher at 60 cm depth compared to 30 cm depth. The higher DOC concentrations at 60 cm may be due to release and transport of the more soluble fraction of organic matter, as also observed with the DOC in the lined cell leachate. Alternatively, the DOC closer to the surface is subject to more rapid biological consumption. The decline in average DOC at 30 cm and 60 cm is perhaps attributable to passing of the DOC front and the readily degradable DOC fraction being consumed by soil organisms. Average  $\text{NH}_4^+$  concentrations range between 589 and 1030

mg kg<sup>-1</sup> at 30 cm with no clear trend over time. The lysimeter data at 60 cm and 90 cm, however, show a general increase in average NH<sub>4</sub><sup>+</sup> concentration with time. Nitrate concentrations were close to the detection limit of 0.01 mg/L at 30 cm and 60 cm depths prior to the emplacement of the biosolids stockpile

Results of the analyses of individual pan lysimeter filtrates sampled in June 2003 are shown in Table 3. The significant differences in concentrations seen at the same depth may be attributed to the existence of the preferential flow paths. The installation of pan lysimeters involves disturbing the existing soil structure, possibly creating preferential flow paths above the lysimeters. Subsurface flow may also be restricted locally by biological growth plugging the open pores and pathways in the soil, as has been reported in landfill leachate column studies (Jensen and Christensen, 1999). Evidence for the preferential flow paths was also the greatly varying yield of liquid from the lysimeters at the three different depths. Lysimeters especially at the 60 cm and 90 cm depth failed to yield as much liquid as lysimeters at the 30 cm depth. Preferential flow paths are commonly found in nature (e.g., worm holes, cracks and roots in soils) and have been documented to accelerate biosolids leaching into soil (Camobreco et al., 1996).

### **Lysimeter – Metals**

Lysimeter results for metals are presented as: (1) average concentrations (composite samples) at a given depth over time (Fig. 5), and (2) one sampling round showing results of each of the 15 individual lysimeter pans sampled in June 2003 after the emplacement of the biosolid stockpile (Table 4). There is a wide range in concentrations for any given metal at the same depth; nevertheless systematic changes are observed with depth and over time.

Concentrations of Fe, Mn, P and Al were in the mg L<sup>-1</sup> range in several of the samples (Table 4). These concentrations were generally lower in the deepest lysimeter at 90 cm. Arsenic concentrations showed a steady increase over time as well as depth, with the highest concentrations at 90 cm (Fig. 5). Cu and Zn concentrations increased in Sept. 2003, possibly due to the emplacement of a fresh biosolid stockpile in July 2003 (Fig. 5). Similar to As, highest Cu concentrations were observed at 90 cm. Soil extractions before the emplacement of the biosolid stockpile showed total As and Cu concentrations of 6.1 and 14.3 µg g<sup>-1</sup>, respectively. Considering a soil bulk density of 2.6 g cm<sup>-1</sup> and porosity ranging between 0.3 and 0.5, the soil

may potentially release two to three orders of magnitude more As and Cu than observed in the lysimeters. Therefore, the observed As and Cu in the lysimeters may indeed be released from the underlying soil. P concentrations showed a slight increase over time with highest concentrations at the 30 cm depth (Fig. 6), suggesting that biosolids are the source of P, and that the underlying soil and/or microorganisms act as a sink for P. Concentrations of Cd and Ni ranged between 5-20 and 20-250  $\mu\text{g L}^{-1}$ , respectively, and remained relatively constant over time (data not shown here).

## **Conclusions**

Leachate from field stacked biosolids contains significant concentrations of DOC and N, well in excess of typical agronomic demands.  $\text{NH}_4^+$  was the dominant species of N, and organic N, as a minor species, represented approximately 10% of the total dissolved N. Both species contribute to the formation of  $\text{NO}_3^-$  in soil and groundwater. In addition, P is mobilized from the biosolids in the low ppm concentration range.

The results of this study also indicate that Al, Fe, Mn, and As are released from a lime-stabilized Class B biosolids stockpile during the first 90 days, which in this study exceed the annual soil loading limits. The other regulated metals studied (Cd, Cu, Ni, Se and Zn) were released during the first 90 days of stockpiling at rates below annual loading limits. Lysimeter data showed As, Cu, P and Se to be mobile through the soil column in the field. Soil-bound As and Cu were perhaps mobilized due to the presence of the anaerobic environment in the soil as their concentrations increased with depth. Other analytes, such as P and Se showed a general decreased with depth, suggesting that they directly originated from the biosolids.

## **Acknowledgements**

This project was funded by the Maine Department of Environmental Protection and the Maine Water Resources Research Institute with support and collaboration of the Department of the Interior, U.S. Geological Survey and the University of Maine, under Grant No. 01HQGR0083. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Government, or the Maine Department of Environmental Protection. We thank Justin Jamieson, Ken Johnson and Liz Dyzek for their help in the field.

## **References**

- Amirbahman, A.; and Olson, T.M.; "Transport of humic matter-coated hematite in packed beds," *Environ. Sci. Technol.* 27 (1993) 1807-1813.
- Amirbahman, A.; Schönenberger, R.; Furrer, G. and Zobrist, J.; "Experimental study and steady-state simulation of biogeochemical processes in laboratory columns with aquifer material"; *J. Contaminant Hydrol.* 64 (2003) 169-190.
- Balint, A.; Heltai, G.; Notas, E.; Tarr, Z. and Jung, K.; "Modelling of environmental impact of different N-sources in soil/atmosphere system"; *Microchem. J.* 73 (2002) 113-124.
- Barbarick, K, Ippolito, J, and Westfall, D, "Extractable trace elements in the soil profile after years of biosolids application": *J. of Environmental Quality*, 27 (1998) 801-805.
- Basta, N., Ryan, J., and Chaney, R., "Trace element chemistry in residual-treated soil: key concepts and metal bioavailability": *J. of Environmental Quality*, 34 (2005) 49-63.
- Baveye, P.; McBride, M.B.; Bouldin, D.; Hinsley, T.D.; Dahdoh, M.S.A. and Abdel-sabour, M.F.; "Mass balance and distribution of sludge-bourne trace elements in a silt loam soil following long-term applications of sewage sludge"; *Sci. Total Environ.* 227 (1999) 13-28.
- Bell, P.F.; James, B.R. and Chaney, R.L.; "Heavy metal extractability in long-term sewage sludge and metal salt-amended soils"; *J. Environ. Qual.* 20 (1991) 481-486.
- Bergkvist, P.; Jarvis, N.; Berggren, D. and Carlgren, K.; "Long-term effects of sewage sludge applications on soil properties, cadmium availability and distribution in arable soil"; *Agr. Ecosys. Environ.* 2111 (2003) 1-13.
- Berti, W, and Jacobs, L, "Distribution of trace elements in soil from repeated sewage sludge applications": *J. of Environmental Quality*, 27 (1998) 1280-1286.
- Camobreco, V.J.; Richards, B.K.; Steenhuis, T.S.; Peverly, J.H. and McBride, M.B.; "Movement of heavy metals through undisturbed and homogenized soil columns"; *Soil Sci.* 161 (1996) 740-750.
- Cappon, Chris, "Content and chemical form of mercury and selenium in soil, sludge, and fertilizer materials": *Water, Air, and Soil Pollution*, 22, (1984) 95-104.
- Chaney, Rufus, Reeves, Philip, Kukier, Urszula, and others, "Food chain transfers and bioavailability of Cd and other elements in plants grown on biosolids amended soils", *Proc. Sustainable Land Application Conference*, Lake Buena Vista, Florida, January 2004.
- Chang, A.C.; Warneke, J.W.; Page, A.L. and Lund, L.J.; "Accumulation of heavy metals in sewage-sludge treated soils" *J. Environ. Qual.* 13 (1984) 87-91.
- Clapp, C., Larson, W., and Dowdy, R., eds., "Sewage Sludge: Land utilization and the environment, St. Paul, MN (1994).
- Dowdy, R.H.; Latterell, T.D.; Hinesly, R. B.; Grussman, R.B. and Sullivan, D.L.; "Trace metal movement in an Aeric Ochraqualf following 14 years of annual sludge applications"; *J. Environ. Qual.* 20 (1991) 119-123.



Dzombak, D.A.; and Morel, F.M., "Surface Complexation Modeling: Hydrous Ferric Oxide," Wiley, New York, 1990.

Estes, George, and Buob, Thomas, (2001), Agronomic and environmental aspects of biosolids on corn production in New Hampshire: University of New Hampshire, Agricultural Research Station.

Gerritse, R. , Vriesma, R, Dalenberg, J, and others, "Effect of sewage sludge on trace element mobility in soils": Journal of Environmental Quality, 11 (1982) 359-364.

Goody D.C.; Clay J.W.; Bottrell S.H.; "Redox-driven changes in porewater chemistry in the unsaturated zone of the chalk aquifer beneath unlined cattle slurry lagoons"; Appl. Geochem., July 2002, 17, 903-921.

Hall, J., and Williams, J., (1984), The use of sewage sludge on arable and grasslands, Berglund, S., and Davis, R. L'Hermite P., Utilisation of sewage sludge on land: Rates of application and long-term effects of metals, Uppsala.

Hillier, J.E.; "Aquifer Impacts of Nitrogen Applications: A Case Study" Nitrogen in the Environment Sources, Impact Management, University of Maine Seminar October 8, 1993 (QP 535.N1 N587 1993)

Jacobsen, E. (1998); "Effects of land application of composted biosolids on ground water and native vegetation in the New Jersey Pinelands" U.S. Geological Survey Fact Sheet FS-035-97.

Jensen, D.L. and Christensen, T.H.; "Colloidal and dissolved metals in leachates from four Danish landfills"; Water Res. 33 (1999) 2139-2147.

Kellog, Robert, Lander, Charles, Moffitt, David, and others, (2000), Manure nutrients relative to the capacity of cropland and pastureland to assimilate nutrients: Spatial and temporal trends for the United States, U.S. Department of Agriculture.

Lin, H.T.; Wang, M.C. and Li, G.C.; "Complexation of arsenate with humic substance in water extract of compost" Chemosphere 56 (2004) 1105-1112.

Lovley, D.R. and Phillips, E.J.P., "Novel mode of microbial energy metabolism: organic carbon oxidation coupled to dissimilatory reduction of iron and manganese"; Appl. Environ. Microbiol. 54 (1988) 1472-1480.

Krauskopf, K.B. and Bird, D.K., "Introduction to Geochemistry," 3<sup>rd</sup> ed., McGraw-Hill, New York, 2003.

Maeda, M.; Zhao, B.; Ozaki, Y.; and Yoneyama, T.; "Nitrate leaching in an Andisol treated with different types of fertilizer"; Environ. Pollut. 121 (2003) 477-487.

Martinez C.E.; Jacobson, A.R. and McBride, M.B.; "Aging and temperature effects on DOC and elemental release from metal contaminated soils"; Environ. Pollut. 122 (2003) 135-143.

Maticic, B.; "The impact of agriculture on ground water quality in Slovenia: standards and strategy"; Agr. Water Manag. 40 (1999) 235-247

McBride, Murray, Richards, Brian, Steenhuis, Tammo, and others, "Mobility and solubility of toxic metals and nutrients in soil fifteen years after sludge application": Soil Science, 162, (1997) 487-500.

McBride, M.B.; “Soluble trace metals in alkaline stabilized sludge products”; J. Environ. Qual. 27 (1998) 578-584.

McBride, M.B.; Richards, B.K.; Steenhuis, T. and Spiers, G.; “Long-Term Leaching of Trace Elements in a Heavily Sludge-Amended Silty Clay Loam Soil”; Soil Sci. 164 (1999) 613-623.

McBride, M. , Richards, B., and Steenhuis, T., “Bioavailability and crop uptake of trace elements in soil columns amended with sewage sludge products”: Plant and Soil, 262 (2004) 71-84.

McDowell, W.H. and Chestnut, T.J.; “Final Report to DES and NH Legislature, June 1998 – November 2001 Monitoring Demonstration at a Top-Soil Manufacturing Site in New Hampshire” March 15, 2002.

McGrath, S.P. and Lane, P.W.; “An explanation for the apparent loss of metal in a long-term field experiment with sewage sludge”; Environ. Pollut. 60 (1989) 235-256.

Merrington, G., Oliver, I., Smernik, R., and others, “The influence of sewage sludge properties on sludge-borne metal availability” : Advances in Environmental Research, 8 (2003) 21-36

[Compendium of Maine Regulations \(CMR\), Chapter 419 Agronomic Utilization of Residuals, www.maine.gov/sos/cec/rcn/apa/06/096/096c419.doc](http://www.maine.gov/sos/cec/rcn/apa/06/096/096c419.doc)

National Research Council; “Biosolids Applied to Land: Advancing Standards and Practices” July 2, 2002.

Peckenham, J.M., J. Nadeau, J. and A. Amirbhaman, “Nitrogen Release from Field Stack Biosolids”, BioCycle, 46 (2005) 47-52.

Peckenham, J.M. (2005) Beneficial Reuse of Biosolids: A Review, prepared for Maine State Planning Office and the Maine Waste Water Control Association, March 2005, 70 p.

Qureshi, S.; Richards, B.K.; Hay, A.G.; Tsai, C.C., McBride, M.B.; Baveye, P. and Steenhuis, T.S.; “Effect of Microbial Activity on Trace Element Release from Sewage Sludge” ; Environ. Sci. Technol. 37 (2003) 3361-3366.

Redman, A.D., MaCalady, D.L., and Ahmann, D.; “Natural Organic Matter Affects Arsenic Speciation and Sorption onto Hematite” Environ. Sci. Technol. 36 (2002) 2889-2896.

Richards, B. K.; Steenhuis, T. S.; Peverly, J. H. and McBride, M. B.; “Metal mobility at an old heavily loaded sludge application site”; Environ. Pollut. 99 (1998) 365-377.

Richards, Brian, Schulte, Brenda, Heilig, Arik, and others, “Environmental impacts of applying manure, fertilizer, and sewage biosolids on a dairy farm”: J. of the American Water Resources Association, 4 (2004) 1025-1042.

Roelle, P.A.; Aneja, V.P.; Mathur, R.; Vukovich, J. and Peirce, J.; “Modeling nitric oxide emissions from biosolids amended soils”; Atmos. Environ. 36 (2002) 5687-5696.

Shober, A., Stehouwer, R., and McNeal, K., (2002) Agricultural utilization of biosolids in Pennsylvania: Assessment of biosolids effects on soil and crop quality: Pennsylvania Department of Environmental Protection.

Sloan, J, Dowdy, R, and Dolan, M, “Recovery of biosolids-applied heavy metals sixteen years after application”: J. of Environmental Quality, 27 (1998) 1312-1317.

Smith, K.A. and Frost, J.P.; “Nitrogen excretion by farm livestock with respect to land spreading requirements and controlling nitrogen losses to ground and surface waters. Part 1: cattle and sheep”; *Bioresour. Technol.* 71 (2000) 173-181.

Smith, S. R.; Woods, V. and Evans, T.D.; “Nitrate dynamics in biosolids-treated soils:I. Influence of biosolids type and soil type” *Bioresour. Technol.* 66 (1998a) 139-149.

Smith, S.R.; Woods, V. and Evans, T.D.; “Nitrate dynamics in biosolids-treated soils III: Significance of the organic nitrogen, a twin-pool exponential model for nitrogen management and comparison with the nitrate production from animal wastes”; *Bioresour. Technol.* 66 (1998b) 161-174.

Speir, T., Van Schaik, A., Percival, H., and others, “Heavy metals in soil, plants and groundwater following high-rate sewage sludge application to land”: *Water, Air, and Soil Pollution*, 150 (2003) 319-358.

Stadelmann, F., and Furrer, O., (1985) Long-term effects of sewage sludge and pig slurry applications on microbiological and chemical soil properties in field experiments, Williams, J., Guidi, G., and L'Hermite, P., Long-Term effects of sewage sludge and farm slurries applications, Pisa.

Stevens, Michael, Yager, Tracey, Smith, David, and others, (2003) Biosolids, soils, ground-water, and streambed-sediment data for a biosolids application area near Deer Trail, Colorado, 1999.: Denver, CO, U.S. Geological Survey.

Stukenberg, John, Carr, Scott, Jacobs, Lee, and others, (1993) Document long-term experience of biosolids land application programs: Alexandria, VA, Water Environment Research Foundation.

Stumm, W. and Morgan, J.J., “Aquatic Chemistry,” 3<sup>rd</sup> ed., Wiley-Interscience, New York, 1996.

Tipping, E., “Cation binding by Humic Substances,” Cambridge University press, Cambridge, UK, 2002

U.S. Environmental Protection Agency, 2000, U.S. Environmental Protection Agency, Guide to field storage of biosolids: Washington, DC, U.S. Environmental Protection Agency.

US Environmental Protection Agency [Part 503 Rule, http://www.epa.gov/owm/mtb/biosolids/503pe/index.htm](http://www.epa.gov/owm/mtb/biosolids/503pe/index.htm)

von Gunten, U. and Schneider, W.; “Primary products of the oxygenation of the iron(II) at an oxic-anoxic boundary: nucleation, aggregation and aging”; *J. Colloid Interface Sci.* 145 (1991) 127-139.

von Gunten, U. and Zobrist, J.; “Biogeochemical changes in groundwater infiltration systems: column studies”; *Geochim. Cosmochim. Acta* 57 (1993) 3895-3906.

Wang, Min-Jiang, McGrath, Steve, and Jones, Kevin, “Chlorobenzenes in field soil with a history of multiple sewage sludge applications”: *Environmental Science and Technology*, 29 (1995) 356-362

Welch, A.H. and Stollenwerk, K.G.; “Natural Remediation Potential of Arsenic Contaminated Ground Water” in “Arsenic in Ground Water” edited by A.H. Welch and K.G. Stollenwerk, Kluwer Academic Publishers (2003) 351-380.

Yingming, L. and Corey, R.B.; "Redistribution of soil-borne cadmium copper and zinc in a cultivated plot"; J. Environ. Qual. 22 (1993) 1-8

**Table 1 – Sample Analytes by Matrix**

<b>Sample Location</b>	<b>Biosolids</b>	<b>Leachate/Runoff</b>	<b>Lysimeter</b>	<b>Soil</b>
Sampling Frequency	Pre- and Post Test	3 to 14 days	monthly	Pre- and Post test
TKN	×	×	×	×
NO <sub>3</sub> <sup>-</sup>	×	×	×	×
NO <sub>2</sub> <sup>-</sup>	×	×	×	×
NH <sub>4</sub> <sup>+</sup>	×	×	×	×
Organic Carbon	TOC	DOC	DOC	TOC
COD		×	×	
Metals	×	×	×	×
pH	×	×	×	×
Percent Solids	×			

**Table 2 – Nitrogen and COD concentrations in the leachate of lined cells**

<b>Time (Days)</b>	<b>Cumulative Flow (L)</b>	<b>COD (mg/L)</b>	<b>NO<sub>2</sub><sup>-</sup> (mg/L)</b>	<b>NO<sub>3</sub><sup>-</sup> (mg/L)</b>	<b>NH<sub>4</sub><sup>+</sup> (mg/L)</b>	<b>TKN (mg/L)</b>	<b>DOC (mg-C/L)</b>
6	49	20300	0	0.203	1860	2260	3900
19	4702	33125	0.036	0.134	2795	2944	8100
26	7034	36725	0.019	0.142	3168	3414	8900
29	12069	37525	0.025	0.087	3471	3693	8600
36	18297	36550	0.023	0.113	3939	3936	8100
50	26394	35400	0.022	0.089	3894	4275	8100
61	31353	30850	0.033	0.082	4120	4797	7900
83	34368	25250	0.039	0.137	4416	4826	6000
90	35888	27200	0.067	0.194	4832	4893	6800
100	38243	24000	0.042	0.110	4602	5085	7000

**Table 3 – Zero tension pan lysimeter filtrate test results June 2003**

<b>Lysimeter</b>	<b>DOC (mg/L)</b>	<b>COD (mg/L)</b>	<b>NO<sub>2</sub><sup>-</sup> (mg/L)</b>	<b>NO<sub>3</sub><sup>-</sup> (mg/L)</b>	<b>NH<sub>4</sub><sup>+</sup> (mg/L)</b>	<b>TKN (mg/L)</b>
1C1	67	1810	0.074	N.D.	167	223
1C2	725	6520	0.102	N.D.	600	715
1C3	1270	12660	0.218	N.D.	2400	2590
1E1	79	120	N.D.	N.D.	23.5	38.8
1E2	2030	20225	0.552	0.036	1960	2420
2C1	4860	26700	0.443	0.031	2384	2840
2C2	301	2690	0.062	N.D.	257	358
2C3	55	384	0.012	N.D.	87.8	112
2E1	6060	16075	0.036	N.D.	1340	3030
2E2	76	1680	0.031	N.D.	149	198
3C1	24	17	0.802	23.7	0.34	27.2
3C2	270	3480	N.D.	N.D.	342	468
3C3	54	246	12.5	8.8	0.88	24.6
3E1	39	54	1.0	43.1	1.19	52.5
3E2	37	422	N.D.	0.012	22.8	37.3

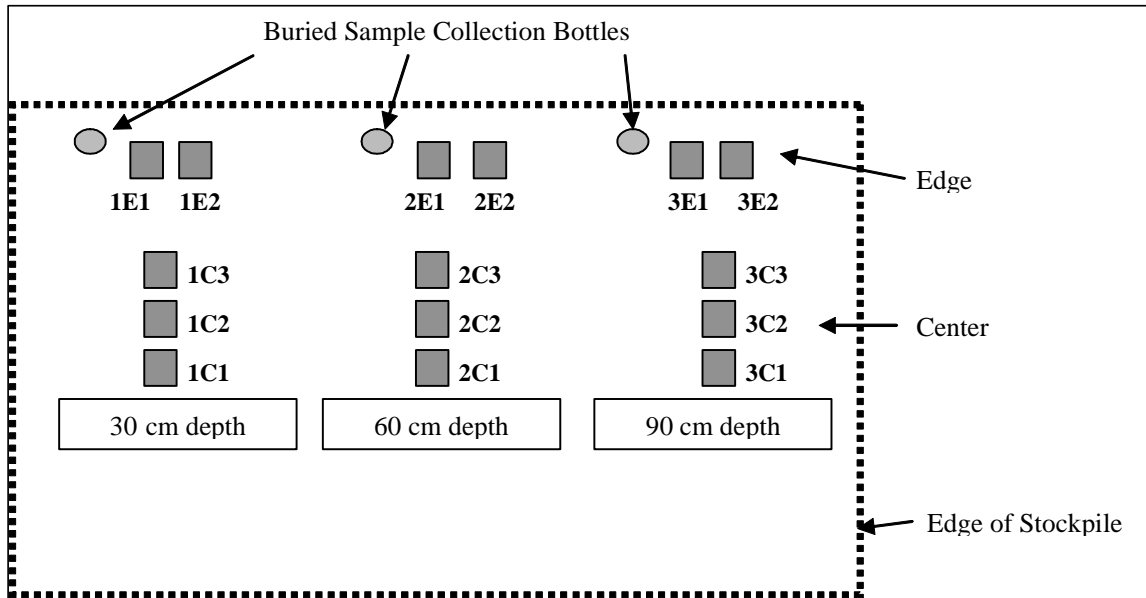
See Figure 1 for the location of the lysimeters.

**Table 4 – Zero tension pan lysimeter metal concentrations June 2003**

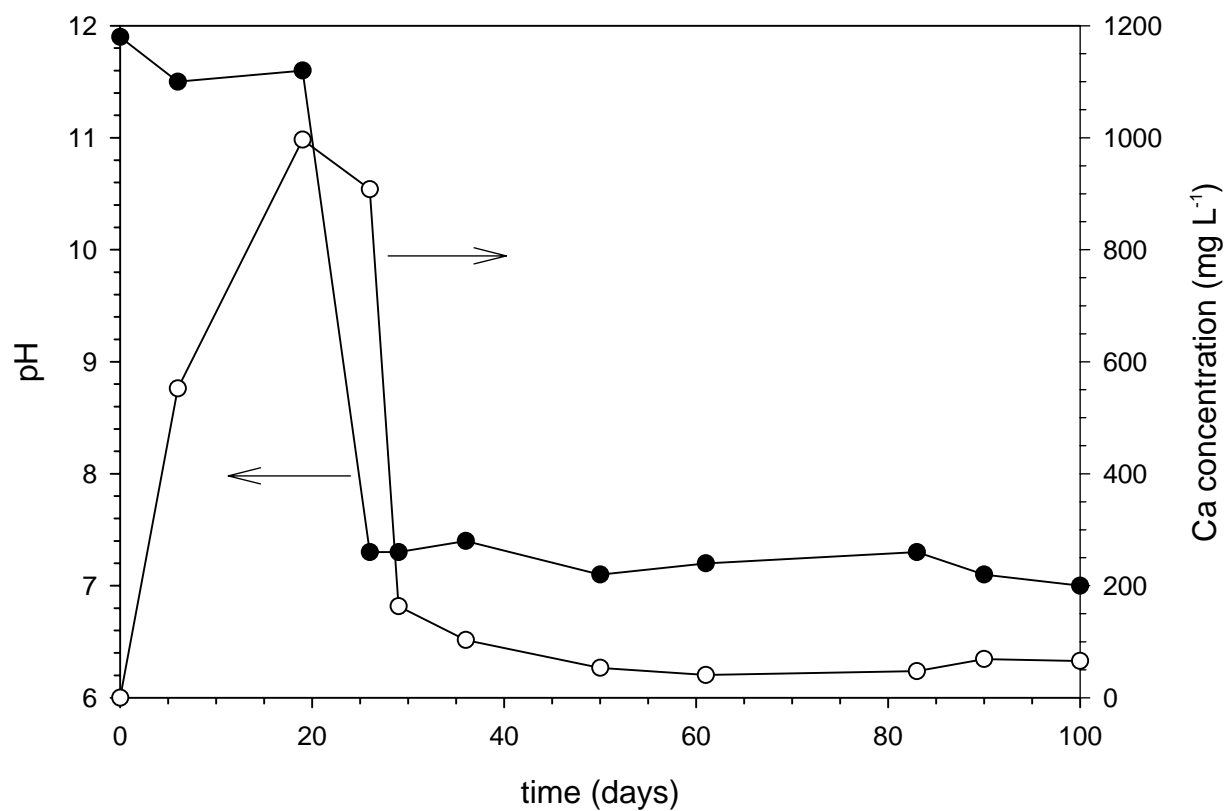
<b>Lysimeter</b>	<b>Al (mg/L)</b>	<b>As (mg/L)</b>	<b>Cd (mg/L)</b>	<b>Cu (mg/L)</b>	<b>Fe (mg/L)</b>	<b>Mn (mg/L)</b>	<b>Ni (mg/L)</b>	<b>P (mg/L)</b>	<b>Se (mg/L)</b>	<b>Zn (mg/L)</b>
1C1	471	23.7	40.1	236.4	537	195	35.6	2761	79.9	28.2
1C2	930	43.8	0.5	70.1	41370	9415	145.8	2956	118.1	42.9
1C3	1613	128.0	8.1	291.8	10558	3564	307.6	10919	263.0	84.4
1E1	140	1.8	58.7	18.7	55	0	0	144	3.3	11.7
1E2	3248	302.2	3.4	167.5	47905	5049	474.1	28686	391.0	175.0
2C1	2518	267.7	8.5	246.6	53898	44032	500.4	21265	286.6	171.6
2C2	488	38.5	12.9	167.3	428	1184	82.3	1255	99.6	20.8
2C3	156	33.8	4.4	89.2	133	53	0.5	464	36.4	20.2
2E1	2802	134.5	0.4	507.8	82732	32654	514.4	3273	244.5	214.9
2E2	385	31.1	0	99.2	328	230	36.4	881	78.3	21.1
3C1	116	58.9	38.6	0.9	12	0	0	286	55.4	232.8
3C2	631	123.9	6.6	513.3	551	447	136.6	2165	194.2	115.0
3C3	135	33.7	36.7	17.5	31	0	0	112	59.4	78.1
3E1	179	60.0	9.6	14.8	76	5	0.5	670	64.0	43.6
3E2	156	26.9	5.8	23.9	84	14	10.0	121	57.1	45.0

See Fig. 1 for the location of the lysimeters.

**Figure 1 – Lysimeter plot schematic –Lysimeters were labeled with a 3 digit code D-L-N where D was depth (1 = 30 centimeters, 2 = 60 centimeters and 3 = 90 centimeters), L was location (C=center E=edge) and N was a serial number 1 through 3**

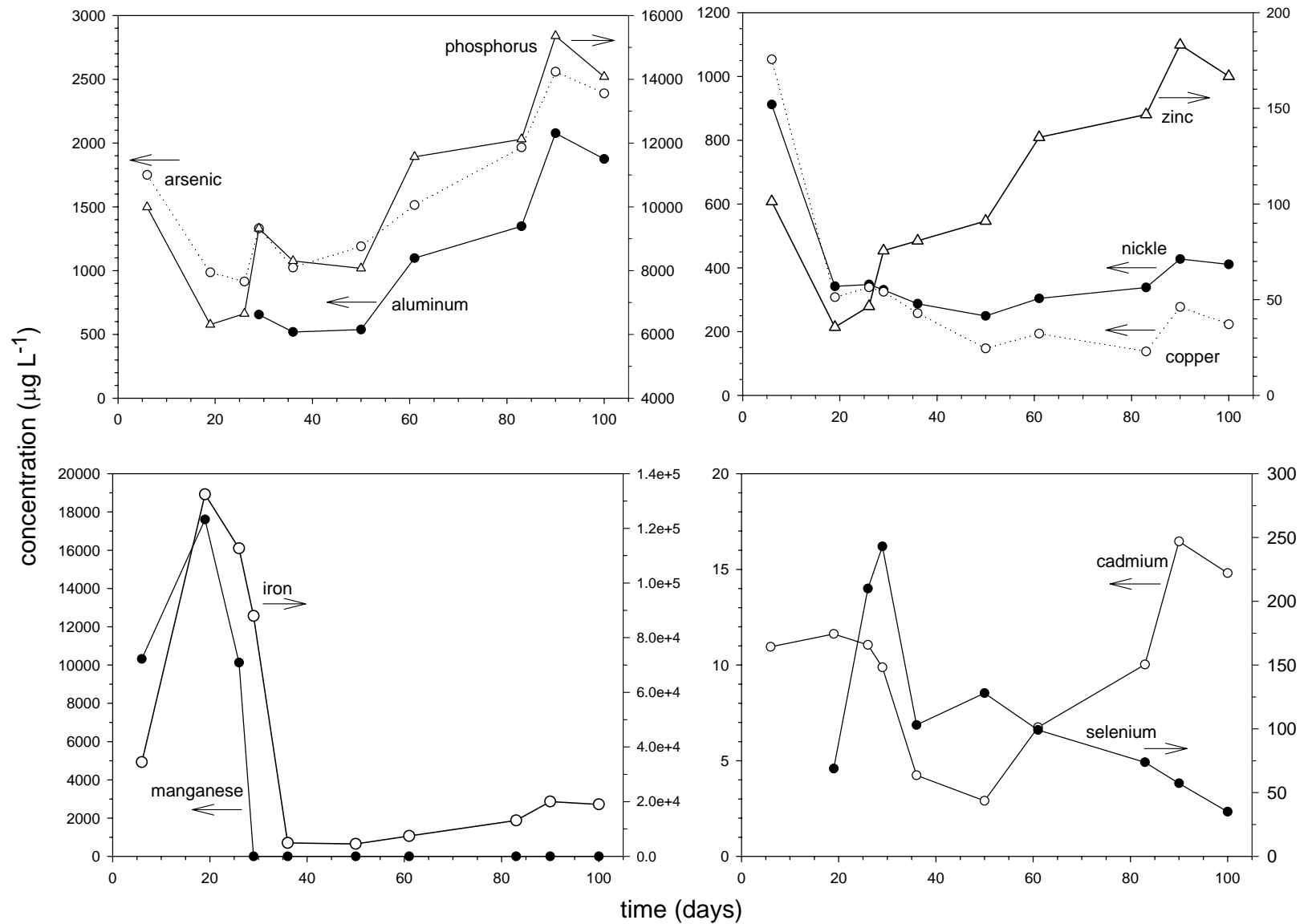




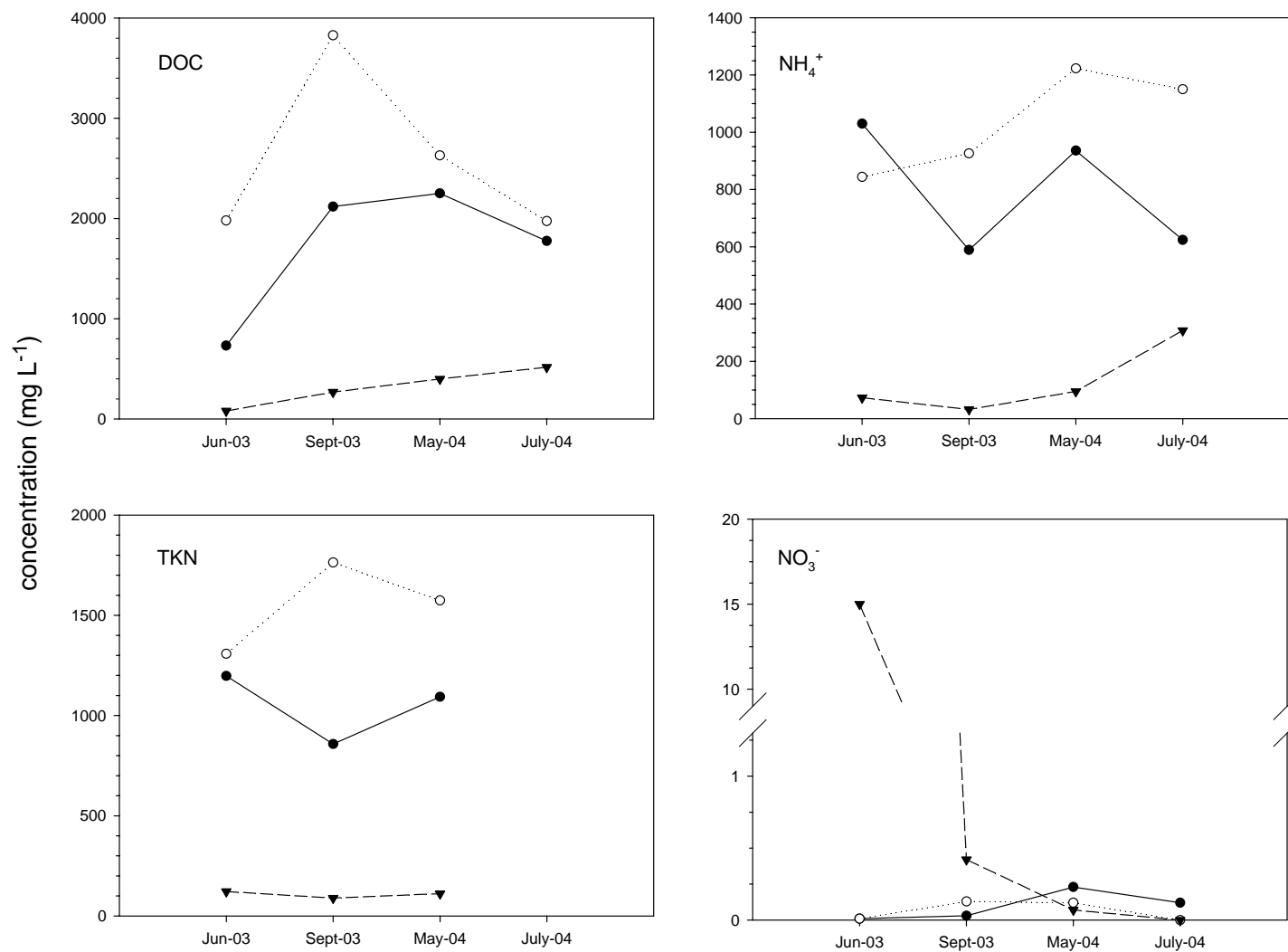


**Figure 3 – Lined cell biosolids pH and lined cell leachate Ca concentration from July 9, 2003 to October 17, 2003.**

**Figure 3 – Lined cell leachate trace metal concentration from July 9, 2003 to October 17, 2003.**



**Figure 4 – Zero-tension pan lysimeter DOC,  $\text{NH}_4^+$ , TKN and  $\text{NO}_3^-$  average concentrations 2003 – 2004.**



**Figure 5 – Zero-tension pan lysimeter temporal average concentrations of As, Cu, Zn and Se at depth from 2003 to 2004.**

